Mg^{2+}-doped poly(ε-caprolactone)/siloxane biohybrid electrolytes

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Abstract Electrolytes based on a poly(ε-caprolactone) (PCL)/siloxane organic/inorganic host framework doped with magnesium triflate ($Mg(CF_3SO_3)_2$) were synthesized by the sol-gel process. In the biohybrid matrix short PCL chains are covalently bonded via urethane linkages to the siliceous network. In this study the salt content of samples was identified using the conventional n notation, where n indicates the number of ($C(=O)(CH_2)_5O$) PCL repeat units per Mg^{2+} ion. Materials with compositions ranging from n=∞ to 2 were prepared. The only composition prepared that is not entirely amorphous is that with n = 1. Xerogels with n ≥ 7 are thermally stable up to up to at least 200 ºC. The most conducting ormolyte of the series is that with n = 26 ($5.9x10^{-9}$ and $9.8x10^{-7}$ Scm^{-1} at 24 and 104 ºC, respectively).

Keywords poly(ε-caprolactone)/siloxane biohybrid, magnesium triflate, ionic conductivity, thermal analysis

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1. Introduction

Polymer electrolytes (PEs) [1] are attractive materials for the fabrication of solid-state electrochemical devices, particularly rechargeable batteries, capacitors and sensors [2]. A remarkable number of studies have been carried out on PEs based on poly(oxyethylene) (POE), or host polymers with a similar structure, incorporating guest salts with monovalent cations [2]. Although lithium ion conducting electrolytes are of special interest because of potential application in solid-state lithium (Li) batteries, their commercial success is conditioned by certain drawbacks associated with the high reactivity of this alkaline metal (e.g. dentritic deposition of Li, growth of passive layer on Li surface and safety issues).

Magnesium (Mg) may be a good alternative to Li. This alkaline-earth metal is located close to Li in the electrochemical series (electrode potential of -2.37 V vs. SHE) and has good electrochemical performance (high electrochemical equivalence of 2.2 Ahg^{-1}). Owing to these merits, Mg has already been successfully employed as anode in primary and reserve batteries [3]. Rechargeable solid state Mg batteries have been, however, less investigated. As a basis for commercial cells, Mg has several advantages with respect to Li. Unlike Li, the mineral resources of which are limited and localized, Mg raw resources are abundant and as a consequence are cheaper than Li. Moreover, Mg is non-toxic and hence environmentally friendly. As this metal is less reactive than Li towards oxygen and water, it may be handled safely in open air and hazards are minimized. The ionic radii of Li^+ and Mg^{2+} are comparable in magnitude (68 and 65 ppm, respectively), which means that Mg-based batteries may use the same insertion compounds that have already been developed for Li cells. Aurbach et al. [4] demonstrated that the use of Mg for the fabrication of rechargeable solid state batteries is indeed very promising.

Mg rechargeable solid-state batteries require Mg^{2+} conducting PEs with high room temperature ionic conductivity. In contrast with the large number of publications dealing

with the characterization of Li^+-doped PEs, only a reduced number of studies concern materials incorporating Mg^{2+}.

Several authors reported the synthesis and properties of conventional PEs composed of POE (or a poly(ethylene glycol) (PEG)) and magnesium thiocianate ($Mg(SCN)_2$) [5], magnesium perchlorate ($Mg(ClO_4)_2$) [5,6] or magnesium chloride ($MgCl_2$) [7-12]. The effect of plasticizers on POE-based electrolyte systems containing magnesium triflate ($Mg(CF_3SO_3)_2$) was studied by Kumar and Munichandraiah [13]. Jeong et al. investigated electrolytes based on poly(vinyl alcohol) and $Mg(CF_3SO_3)_2$ [14]. Di Noto et al. characterized doped esters of ethylenediaminetetracetic acid and polyethylene glycol [15] and an alternated copolymer based on α-hydro-ω-oligo(oxyethylene)hydroxyl-poly[oligo(oxyethylene)oxydimethylsililene] with $MgCl_2$ [16,17]. Systems incorporating POE-containing blends and $Mg(CF_3SO_3)_2$ were also studied [18]. A host polymer system based on an oligo(oxyethylene)-grafted polymethylmethacrylate (PMMA) matrix and a linear polyether was doped with $Mg(CF_3SO_3)_2$, $Mg(ClO_4)_2$ and magnesium bis(trifluoromethanesulfonyl)imide ($Mg[N(SO_2CF_3)_2]_2$) [19,20]. Polymeric electrolytes consisting of POE-modified PMMA, an organic plasticizer and $Mg(CF_3SO_3)_2$ and $Mg(ClO_4)_2$ were investigated by Morita et al. [21]. Many efforts have been devoted to the development of gel polymer electrolytes (GPEs) incorporating magnesium salts [22-33].

Very little attention has been dedicated, however, to Mg^{2+}-doped organic/inorganic hybrid [34] electrolytes (usually known as *ormolytes* - organically modified silicate electrolytes) prepared *via* the sol-gel method [35]. This *soft* chemical synthetic process permits the preparation, under mild reaction conditions, of electrolytes with a large variety of molded shapes and with improved features. In POE/siloxane hybrid materials the amorphous character, the good mechanical resistance and the excellent thermal/chemical stability provided by the inorganic backbone coexist with the flexibility and solvating

ability characteristic of organic chains. These host hybrid networks also admit considerably higher guest salt concentrations than those possible in classical systems.

Mitra and Sampath were the first to introduce a family of hybrid materials doped with a magnesium salt [36]. These authors described a Class I matrix derived from tetraethylortosilicate and PEG to which $Mg(ClO_4)_2$ and $MgCl_2$ were added. More recently our group prepared and characterized a novel series of Class II di-urea cross-linked POE/siloxane ormolytes doped with $Mg(CF_3SO_3)_2$ [37]. Infrared and Raman spectroscopies were used to elucidate the ionic conductivity/ionic association relationship [38].

Encouraged by the high thermal stability (up to at least 300 ºC for n > 0.5), the moderate ionic conductivity levels ($1.6x10^{-7}$ and $3.2x10^{-5}$ Scm^{-1} at 25 and 100 ºC, respectively, at n = 0.5) and the good electrochemical stability (7 V *versus* Li/Li^+ at n = 0.5) exhibited by the family of amorphous di-urethane cross-linked poly(ε-caprolactone) (PCL(530))/siloxane ormolytes (where 530 represents the average molecular weight) doped with $LiCF_3SO_3$ [39], we decided to extend the previous study to include the d-PCL(530)/siloxane-based biohybrid system doped with $Mg(CF_3SO_3)_2$. The thermal properties and ionic conductivity of a series of samples with a wide salt concentration range ($\infty > n \geq 1$) have been examined. To the best of our knowledge, this is the first time that PCL is studied as a basis for Mg^{2+} conducting electrolytes.

PCL is a linear, aliphatic thermoplastic, biocompatible, permeable, hydrophobic and biodegradable poly(ester), non-toxic for living organisms. This polymer is degraded slowly by hydrolysis of ester linkages and resorbed, under suitable physiological conditions, over a fairly extended period. PCL and its copolymers have therefore found widespread application in medicine [40-42]. Tian et al. [43,44] produced PCL(2000)/silica ceramers to be used as degradable bioglasses, as coating materials for bone implants and prosthetic devices, and as supports for enzyme immobilization. A bioactive and degradable PCL/silica hybrid, with application as a bone substitute, was also proposed by S-H. Rhee et al. [45]

The use of biological polymers (or biopolymers), such as synthetic PCL, is of the great interest in the context of the development of electroactive polymers (EAPs) which include PEs (ion conductors) and conducting electrodes (electronic conductors). EAPs are a new class of materials that is finding application in biosensors, environmentally sensitive membranes, artificial muscles, actuators, corrosion protection, electronic shielding, optical displays, solar materials and components in high-energy batteries [46]. Most bio-derived EAPs are ion conducting materials.

2. Experimental

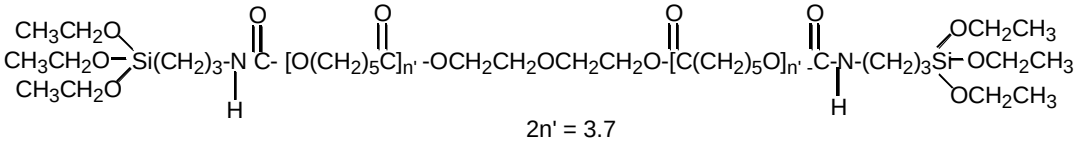
2.1 Materials

Magnesium trifluoromethanesulfonate (usually designated as magnesium triflate, $Mg(CF_3SO_3)_2.xH_2O$ Aldrich) was dried under vacuum at 25 ºC for several days prior to being used. α,ω-hydroxyl poly(ε-caprolactone) (PCL(530), Fluka, average molecular weight 530 g/mol) and 3-isocyanatepropyltriethoxysilane (ICPTES, 97%, Fluka) were used as received. Ethanol (CH_3CH_2OH, Merck) and tetrahydrofuran (THF, Merck) were stored over molecular sieves. High purity distilled water was used in all experiments.

2.1.1 Synthesis of the d-PCL(530)/siloxane$_n$Mg(CF$_3$SO$_3$)$_2$ hybrids

A series of non-doped and $Mg(CF_3SO_3)_2$-doped d-PCL(530)/siloxane hybrid samples were prepared according to a procedure described in detail elsewhere [39]. The synthesis of the host d-PCL(530)/siloxane hybrid involved two steps. In the first stage a urethane cross-link was formed between the hydroxyl (-OH) end groups of the PCL(530) chains and the

isocyanate (-N=C=O) groups of ICPTES in THF at 70-80 ºC to yield the non-hydrolyzed d-PCL(530)/siloxane hybrid precursor:



In the second stage of the synthetic procedure appropriate amounts of CH_3CH_2OH and water were added to this solution to promote the characteristic sol-gel reactions (i.e., hydrolysis and condensation). The guest magnesium salt was incorporated in the latter stage. The materials were obtained as transparent, flexible monoliths with a slightly yellowish hue (Fig. 1). Xerogels with n = ∞, 51, 34, 17, 7, 2 and 1 were produced. We note that these values represent the real concentration of $Mg(CF_3SO_3)_2$ in each sample, as we subtracted from the mass of the salt weighted in each case the mass of the five bonded water molecules present in its formula (see Section 3.1.). The ormolytes were identified using the notation d-PCL(530)/siloxane$_n$[$Mg(CF_3SO_3)_2(H_2O)$].4H_2O. Details of the synthetic procedure are provided in Tables 1 and 2.

2.2 Experimental techniques

2.2.1. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

Samples for thermogravimetric studies were transferred to open platinum pans and analysed using a TA Instruments Q50 thermobalance at a heating rate of 10º min^{-1} using dried nitrogen (N_2) as purge gas (50 ml/min). Prior to measurement, the samples were vacuum-dried over phosphorus pentoxide (P_2O_5) for several days.

A DSC131 Setaram Differential Scanning Calorimeter was used to determine the thermal characteristics of the ormolytes. Disk sections with masses of approximately 15 mg

were removed from the biohybrid film, placed in 30 µl aluminium cans and stored in a dessicator over P_2O_5 for one week at room temperature under vacuum. After this pre-treatment the cans were hermetically sealed and the thermograms were recorded. Each sample was heated from 25 to 300 ºC at 10 ºC min^{-1}. The purge gas used was high purity N_2 supplied at a constant 35 cm^3 min^{-1} flow rate.

2.2.2 Complex impedance measurements

Prior to characterization of conductivity behavior, the ormolytes were vacuum-dried at 80ºC for about 48 h and stored in a high-integrity, argon-filled glove box. For bulk conductivity measurements, an ormolyte disk was placed between two 10 mm diameter ion-blocking gold electrodes (Goodfellow, >99.9%). The electrode/ormolyte/electrode assembly was secured in a suitable constant-volume support, which was installed in a Buchi TO 51 tube oven. A calibrated type K thermocouple, placed close to the ormolyte disk, was used to measure the sample temperature with a precision of about ±0.2 ºC and samples were characterized over a temperature range of between 25 and 100 ºC. Bulk conductivities of the samples were obtained during heating cycles using the complex plane impedance technique (Schlumberger Solartron 1250 frequency response analyzer and 1286 electrochemical interface) over a frequency range of 65 kHz to 0.5 Hz. The electrolyte behavior was found to be almost ideal and bulk conductivities were extracted in the conventional manner from impedance data by using an equivalent circuit composed of R_b in parallel with C_g, where R_b is the electrical resistance of the electrolyte and C_g is its geometric capacity. The circuit element corresponding to the blocking electrode interface was simulated by a series C_{dl} element, where C_{dl} in the double layer capacity. The experimental spectra showed a high frequency semicircle with a low frequency vertical spike. Reproducibility of measurements was better than 5%.

3. Results and discussion

3.1. Thermal stability

Close analysis of the TGA curve of the guest salt reproduced in Fig. 2 leads us to conclude that the first loss of mass observed ($T_{onset} \approx 60$ ºC) corresponds to the release of four water molecules and that the second loss of mass, less abrupt, occurring between 110 and 150 ºC is due to the removal of a single water molecule. We may infer from these results that, unlike the four water molecules initially lost, the latter water molecule interacts strongly with the alkaline-earth cation, indicating that it belongs to the first coordination shell of Mg^{2+}. Two of the three endothermic events detected below 170 ºC in the DSC curve of the salt (Fig. 3) may be correlated with the loss of the four labile water molecules: the low temperature weak, ill-defined peak centered at 79 ºC ($T_{onset} \approx 70$ ºC and $T_{endset} \approx 100$ ºC) and the prominent peak centered at 135 ºC ($T_{onset} \approx 100$ ºC). The shoulder centered at approximately 141 ºC ($T_{endset} \approx 150$ ºC) is associated with the Mg^{2+}-coordinated water molecule. These findings suggest that the correct formula of the magnesium salt employed is $[Mg(CF_3SO_3)_2(H_2O)].4H_2O$.

The TGA curves of the d-PCL(530)/siloxane$_n$$[Mg(CF_3SO_3)_2(H_2O)].4H_2O$ biohybrids, represented in Fig. 2, show that the incorporation of increasing amounts of the guest magnesium salt into the d-PCL(530)/siloxane matrix destabilizes significantly this host biohybrid structure in a non-oxidizing atmosphere. In all the samples examined thermal degradation is a multi-step process. Based on the assumption that the negligible initial mass loss observed ($\leq$ 5 %) is exclusively associated with the release of solvents, such as adsorbed water or occluded CH_3CH_2OH and/or THF, we may conclude that in samples with n = 51 and 34 the onset of thermal decomposition occurs at approximately 250 ºC, whereas

in the case of the more concentrated xerogels with n = 17 and 7 degradation starts at about 200 ºC (Fig. 2). Further addition of salt (n < 7) is clearly disadvantageous from the thermal stability standpoint, since it results in a progressive loss of mass that begins at fairly low temperatures.

The d-PCL(530)/siloxane-based xerogels with $\infty \leq n \leq 2$ give rise to DSC curves typical of amorphous materials (Fig. 3). In the thermogram of the material with n = 1 (Fig. 3) a series of endothermic peaks reveal the semi-crystalline nature of this sample. XRD measurements [47] performed recently demonstrated that at this salt-rich composition a crystalline complex with unknown stoichiometry is formed. No evidences of the presence of free salt were found, however, in the XRD pattern of d-PCL(530)/siloxane$_1$[$Mg(CF_3SO_3)_2(H_2O)$].$4H_2O$.

3.3. Conducting properties

Low lattice energy salts composed of a polarizing cation and a large anion of delocalized charge are the most adequate salts for the preparation of POE-type PEs [2]. The Mg^{2+} and $CF_3SO_3^-$ ions fulfil both requirements. However, cation diffusion depends critically on the strength of the cation-polymer interaction: although strong bonds are essential for PE formation, labile bonds are necessary for cation mobility. A comparison of the cation transference numbers of POE-based PEs doped with Mg^{2+} ions and the magnitude of the water exchange rate around the aqueous cation (10^5 s^{-1} [2]) suggests that Mg^{2+} interacts strongly with hard polybasic macromolecules, being an immobile ion. Consequently, PEs based on magnesium salts are expected to be essentially anionic conductors. Dc polarization measurents have demonstrated that this prediction is correct [2].

The Arrhenius conductivity plot of the PCL(530)/siloxane$_n$[$Mg(CF_3SO_3)_2(H_2O)$].$4H_2O$ biohybrids is shown in Fig. 4 and the corresponding conductivity isotherms are depicted in Fig. 5.

The curves of Fig. 4 demonstrate that the levels of ionic conductivity exhibited by the $Mg(CF_3SO_3)_2$-doped d-PCL(530)/siloxane-based hybrids are considerably lower than those of the $Mg(CF_3SO_3)_2$-doped di-ureasils introduced previously (maximum conductivity values of $4.0x10^{-6}$ and $6.74x10^{-5}$ Scm^{-1} at 35 and 104 ºC, respectively, at n = 20) [37] and those of the $MgCl_2$- and $Mg(ClO_4)_2$-doped ormolytes investigated by Mitra and Sampath (at room temperature the most conducting samples attain 10^{-7} and 10^{-5} Scm^{-1}, respectively) [36]. The d-PCL(530)/siloxane$_n$$Mg(CF_3SO_3)_2$ biohybrid that exhibits the highest conductivity is that with n = 34 ($5.9x10^{-9}$ and $9.8x10^{-7}$ Scm^{-1} at 24 and 104 ºC, respectively) (Fig. 5). It is noteworthy that below 50 ºC the conductivity displayed by the d-PCL(530)/siloxane framework is higher than that of the samples with n = 51, 7 and 2 (Fig. 4). The conductivity of the non-doped hybrid structure may be tentatively associated with proton hopping between neighbouring urethane groups [48].

The modest ionic conductivity displayed by the d-PCL(530)/siloxane$_n$$Mg(CF_3SO_3)_2(H_2O)$].$4H_2O$ ormolytes may be correlated with the conduction mechanism that occurs in the di-urethane cross-linked d-PCL(530)/siloxane medium which must be substantially different from that found in the di-urea cross-linked POE/siloxane materials [37] and, logically, from that present in conventional POE-based matrices. In fact, the nature of the available host matrix coordinating sites differs drastically in these three types of host structures: (1) Ether oxygen atoms, urethane carbonyl oxygen atoms and ester carbonyl oxygen atoms in d-PCL(530)/siloxane system; (2) Ether oxygen atoms and urea carbonyl oxygen atoms in the POE/siloxane di-ureasils; (3) Ether oxygen atoms in POE-type macromolecules. In-depth infrared and Raman spectroscopic analyses which are underway will hopefully help us to elucidate the species (free ions, ion contact

pairs or charged clusters) responsible for the complicated conductivity behaviour observed in Fig. 5.

4. Conclusions

Mg^{2+}-doped biohybrids based on a PCL(530)/siloxane-based host matrix have been synthesized by the sol-gel method. In practical all-solid state electrochemical devices, although the magnitude of ionic conductivity is undoubtedly of prime importance, other aspects, such as, the thermal, mechanical and electrochemical stabilities, are essential. Thus, in spite of the poor ionic conductivity displayed by the optimal biohybrid material with n = 34, its high thermal stability and good mechanical properties encourage further investment in this d-PCL(530)/siloxane-based biohybrid system which has lower environmental impact that conventional electrolytes used at present in commercial devices. As the nature of the anion plays a major role on the ionic conductivity of PEs, more suitable magnesium salts will be incorporated into the d-PCL(530)/siloxane framework to yield ormolytes with higher ionic conductivity values. The determination of the electrode/electrolyte compatibility in future work is also compulsory.

Acknowledgements

M. Fernandes, P. C. Barbosa and L. C. Rodrigues acknowledge FCT for grants (contracts SFRH/BD/38530/2007, SFRH/BD/22707/2005 and SFRH/BD/38616/2007).

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Fig. 2 TGA curves of the d-PCL(530)/siloxane$_n$Mg(CF_3SO_3)$_2$(H_2O)].4H_2O biohybrids.

Fig. 3 DSC curves of the d-PCL(530)/siloxane$_n$Mg(CF_3SO_3)$_2$(H_2O)].4H_2O biohybrids.

Fig. 4 Arrhenius conductivity plot of the d-PCL(530)/siloxane$_n$Mg(CF_3SO_3)$_2$(H_2O)].4H_2O biohybrids.

Fig. 5 Isotherms of the ionic conductivity versus composition of the d-PCL(530)/siloxane$_n$Mg(CF_3SO_3)$_2$(H_2O)].4H_2O biohybrids.

Tables

Table 1 - Details of the synthetic procedure of the d-PCL(530)/siloxane$_n$Mg(CF_3SO_3)$_2$(H_2O)].4H_2O biohybrids.

Table 2 - Salt concentration of the d-PCL(530)/siloxane$_n$Mg(CF_3SO_3)$_2$(H_2O)].4H_2O biohybrids expressed in different ways.

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